

Shear banding phenomena in a Laponite suspension

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Shear localization in an aqueous clay suspension of Laponite is investigated through dynamic light scattering, which provides access both to the dynamics of the system (homodyne mode) and to the local velocity profile (heterodyne mode). When the shear bands form, a relaxation of the dynamics typical of a gel phase is observed in the unsheared band soon after flow stop, suggesting that an arrested dynamics is present during the shear localization regime. Periodic oscillations of the flow behavior, typical of a stick-slip phenomenon, are also observed when shear localization occurs. Both results are discussed in the light of various theoretical models for soft glassy materials.

Introduction

Under the influence of a shear flow, many complex fluids exhibit the formation of macroscopic bands, parallel to the flow direction and characterized by different local shear rates. This phenomenon is called *shear banding* and is attributed to the presence of a decreasing branch in the stress-shear rate curve: in a controlled shear experiment, it is observed when the stress falls in the interval where the so called flow curve is multivalued. Experimentally, shear banding has mainly been observed in a class of complex fluids, like wormlike micelles [1, 2, 3, 4], colloidal crystals [5], or lamellar surfactant systems [6, 7], where a phase transition associated to the microstructure occurs under flow. As described by various theoretical models [8, 9, 10, 11, 12], in such systems an ordered phase coexists with a disordered one during the shear banding regime.

However, shear banding has also been observed in soft-glassy materials [13], like foams [14, 15], emulsions [16], or glassy suspensions [16, 17, 18], where a homogeneous structure is kept throughout the system. To our knowledge, few experimental results are available in the literature for this class of systems [15, 16, 17, 18], while the microscopic origin of the phenomenon is poorly understood. Soft-glassy materials are characterized by a viscosity that increases many orders of magnitude as time evolves and the gelation process proceeds (*aging* behavior), and have rheological properties typical of soft solids, such as solid-like behavior below a finite yield stress and shear thinning effect [20]. At the microscopic level, the gelation process corresponds to a slowing down of the structural relaxation with the elapsed time, while shear thinning results from the system structural dynamics being accelerated by a shear flow (*shear rejuvenation*).

A shear banding behavior is expected for such systems, due to the presence of a yield stress, that provides a multivalued region in the flow curve. When heterogeneous flow emerges, a band with null local shear rate, flowing as a solid block, may coexist with a band flowing at a finite local shear rate. This behavior has been called shear localization and, according to numerical and theoretical

models [22, 23], is associated to a dynamical transition: an arrested dynamics characterizes the unsheared band, while the sheared band exhibits a liquid-like behavior. Moreover, these works have evidenced the emergence of a fluctuating shear banded flow, a phenomenon also observed in non glassy shear banding systems [24]. In order to describe this fluctuating behavior, a model accounting for intermittent plastic and elastic events has been developed [25, 26]. At the experimental level, a fluctuating shear banded flow has been observed in glassy suspensions [17, 18] and in emulsions [14, 15], while direct investigation of the system dynamics when shear localization occurs is still missing.

Among others, proper candidates for the study of the shear localization phenomena are suspensions of charged anisotropic colloidal particles such as clay, that have been widely investigated both for their important industrial application [29] and as a prototype of glassy systems [30]. In particular, shear localization have been observed in such suspensions through magnetic resonance imaging (MRI) [16, 28] or visualization techniques [17].

In this paper, we investigate the shear localization phenomenon in an aqueous clay suspension of Laponite, a highly thixotropic liquid which undergoes structural arrest. We are both interested in the study of the system dynamics when the shear bands form and in the fluctuating flow phenomenon. The technique that we use is dynamic light scattering (DLS), which provides access both to the dynamics of the system after shear cessation (in the homodyne mode) and to the local velocity profile during the flow (in the heterodyne mode). In particular, once a shear banding profile has been detected, we monitor the evolution of the system dynamics soon after flow cessation in the unsheared band. A relaxation of the dynamics typical of a gel phase is observed, suggesting that an arrested dynamics characterize the flat band. For the investigation of the fluctuating flow instead, the heterodyne mode provides higher spatial and temporal resolution than MRI or other techniques, previously used to detect the velocity profile when a shear banding fluctuating flow occurs in glassy suspensions [17, 18]. We thus observe periodic oscillations in the flow, which are typ-

ical of a stick-slip behavior: a layer reversibly fractures and reheals, fluctuating between a frozen state (slip) and a fluidized state (stick). Our results on the dynamics of the sheared banding system and on the fluctuating behavior of the velocity profile will show strong analogies with the elastoplastic model of Ref. [25], which describes the flow behavior of a yield stress fluid.

Materials and methods

Aqueous Laponite suspensions have been extensively investigated as a model system for glassy suspensions [31, 32, 33] and the rejuvenating effect of a shear flow on the system dynamics have also been studied [34, 35, 36]. Laponite particles are disk shaped with a diameter of 25 nm and 1 nm thickness and get negatively charged on the faces when dispersed in a polar solvent. For our experiments, Laponite powder, provided by Laporte Ltd, is dispersed in ultrapure water at 3% wt concentration and stirred for about 30 min. The obtained suspension, which is optically transparent and initially "liquid", is loaded through a $0.45 \mu\text{m}$ filter into a home made, disk-disk shear cell for DLS measurements. The cell has a glass disk, of diameter $d = 10 \text{ cm}$, as the rotating plate, and an optical window as the static plate. The cell gap is $h = 7 \text{ mm}$ and we fix conventionally the y axis along this direction, corresponding to the velocity gradient direction under flow.

In the set-up we implemented for DLS measurements [37], an incident laser beam (diode pumped solid-state laser, $\lambda = 532 \text{ nm}$, $P = 150 \text{ mW}$) impinges on the sample passing through the optical window. The scattered light pass through the same window and is collected by a mono-mode optical fiber. Optionally, it can interfere with a coherent local oscillator field (heterodyne mode) through a fiber collection apparatus. Collected light is then detected by a photomultiplier and analyzed by a home made software correlator [36]. The scattering geometry is fixed, with a scattering vector $q = 22 \mu\text{m}^{-1}$. We placed the shear cell in order to have the scattering volume positioned at a radial distance of 2.1 cm from the rotational axis.

The shift of the cell allows us to select the position of the scattering volume in the cell gap and the possibility of choosing a heterodyne correlation scheme enables direct access to the detailed velocity profile [38]. Due to Doppler effect, the velocity v of the particles in the scattering volume can indeed be obtained from the frequency ω of the collected oscillating intensity in heterodyne mode: $v = \omega / (q \cos \hat{q} \hat{v})$, where $q \cos \hat{q} \hat{v}$ is fixed by the scattering geometry. The frequency ω is simply obtained as the peak location in the power spectrum of the intensity fluctuations, acquired in a time interval $0 \div T$. The maximum time resolution that we can achieve with this measurement, at a fixed position of the scattering

volume in the gap, is $T = 10^{-2} \text{ s}$, while the spatial resolution is determined by the scattering volume dimensions $\sim 100 \mu\text{m}$.

The dynamics of the system can be investigated through the normalized correlation function of the scattered intensity (homodyne mode) $g^{(2)}(t', t) = \langle I(q, t) I(q, t') \rangle / \langle I(q) \rangle^2$, which is easily represented in terms of the particle correlation function. In particular, homodyne DLS directly probes the intermediate scattering function of the colloidal particles $F_q(t, t') = \langle \rho_{-q}(t) \rho_q(t') \rangle / \langle |\rho_q|^2 \rangle$, which plays a central role in both theoretical and numerical approaches to glassy dynamics: $g^{(2)}(t, t') = 1 + |F_q(t, t')|^2$ [39]. However, due to geometrical decorrelation effects during the flow [40], the intermediate scattering function cannot be detected when the system is under shear. Therefore, we will follow the system dynamics soon after shear cessation and try to deduce some information on its dynamical behavior during the flow. In classical DLS, the correlation function is calculated as an average over the time-origin. In aging systems, this is possible when the experimental acquisition time needed to get a good signal to noise ratio is longer than the characteristic slow relaxation time of the system τ_s and shorter than the time one should wait before changes in τ_s , due to the aging process, are significant. This condition doesn't hold when the aging dynamics is characterized by a very fast evolution, as it happens soon after flow cessation in a shear banding Laponite sample. Therefore, we cannot obtain the intensity correlation function by time averaging and an ensemble average over many rejuvenating experiments is used instead [36]: $g^{(2)}(t_w, t) = \langle I(q, t_w) I(q, t_w + t) \rangle_e / \langle I(q, t_w) \rangle_e^2$, where $\langle \dots \rangle_e$ indicates the ensemble average over several intensity evolutions acquired after cessation of a repeated shear application. Flow stop is taken as the origin of waiting times t_w . We choose the following protocol: a global shear rate $\dot{\gamma}_1$ is applied to the system for a time interval T_1 ; after shear cessation, the intensity fluctuations are collected for a time interval T_0 with a time resolution of dt ; then a shear rate of the same value $\dot{\gamma}_1$ is applied for T_1 and the cycle starts again. The intensity autocorrelation function is then calculated in the time window $dt \div T_0$, as an ensemble average over all the bunches of counts.

Results I. Investigating the dynamics

When a shear rate of the order of 1 s^{-1} is applied to Laponite samples that have reached dynamical arrest, shear localization phenomenon is often observed, as shown in the inset of Fig. 1. Here the velocity profile along the cell gap, measured through heterodyne DLS, is plotted: a flat band forms next to the static window, while wall slip occurs at both sides. According to theoretical models [22, 23], soft glassy materials exhibiting shear localization are characterized by an arrested dynamics in

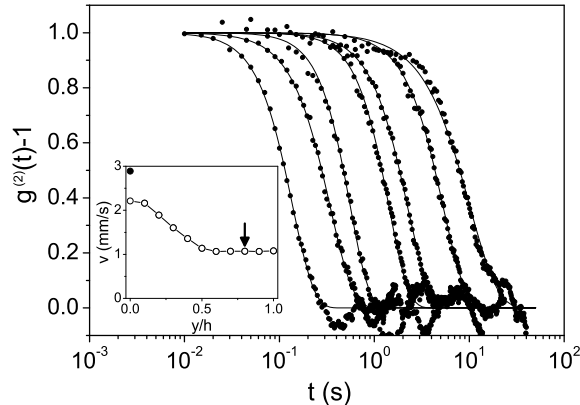


FIG. 1: Normalized intensity autocorrelation functions measured in the flat band soon after shear cessation. Correlation functions are obtained through an ensemble average over many shearing experiments for 7 logarithmically equidistant waiting times t_w between 3 s and 67 s (from left to right) after shear cessation. A compressed exponential fit $\exp[-(t/\tau_s)^\beta]$ is also plotted for each curve. The β parameter fluctuates between 1 and 2. In the *inset*, the velocity profile of the fluid during the experiment is reported and the arrow represents the position of the scattering volume where the measurements were performed. The full circle represents the plate velocity to evidence the presence of wall slip.

the unsheared band. We thus want to investigate the dynamics of our sample in the flat band. As we cannot access directly the dynamical behavior of the system during the flow, we will follow the dynamics in the flat band after shear cessation and then deduce some information on the shear localization regime.

Through the acquisition method explained above, we monitor the evolution of the correlation functions with the waiting time since flow stop, as shown in Fig. 1. These data seem to evidence an aging behavior after shear cessation, as if the flow had a rejuvenating effect on the dynamics of the flat band. However, a null shear rate is not supposed to modify the structure of the system and induce an acceleration of the structural dynamics [21]. In order to exclude that the observed behavior is due to any residual shear rate in the flat band, we monitor the dynamics after the application of a small strain to a gelled sample. In this case, the flow should not modify the structure of the system, as it is supposed to deform only elastically the material. Therefore, a strain $\Delta x/h = 0.3$ of the duration of 1 s is applied cyclically to a gelled sample and the intermediate scattering function soon after strain application is measured as an ensemble average, following the same procedure already described. As evidenced in Fig. 2, an aging dynamics is still evident after flow cessation, showing that such behavior is not due to a shear rejuvenating effect. Though the structural

relaxation time scales differently with t_w in the two experiments, the intermediate scattering functions exhibit a similar form in the range of t_w here investigated. In particular, all correlation functions are well fitted by a compressed exponential: $\exp[-(t/\tau_s)^\beta]$ with $\beta > 1$ (Fig. 1 and Fig. 2).

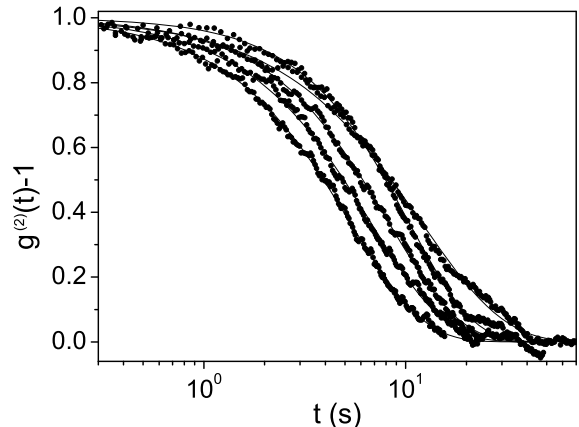


FIG. 2: Normalized intensity autocorrelation functions measured in the flat band soon after the application of a small strain $\Delta x/h = 0.3$. Correlation functions are obtained through the ensemble average procedure for 5 logarithmically equidistant waiting times t_w between 3 s and 17 s after flow cessation. A compressed exponential fit $\exp[-(t/\tau_s)^\beta]$ is also plotted for each curve. The parameter β fluctuates between 1 and 1.5.

Such behavior of the intermediate scattering function can be interpreted, in the light of a model developed to describe anomalous dynamical light scattering in soft glassy gels [41], as due to elastic relaxation of internal stress. In the model, the system behaves as an elastic medium and force dipoles appear at random in space and time, inducing micro-collapses of the structure. The decorrelation of light scattered by the model system is not due to the dynamics of single scatterers, but to a drift mechanism of big aggregates of particles and results in a correlation function of the form $\exp[-(t/\tau)^{1.5}]$. Also an aging behavior is accounted for by the model, where it is interpreted in terms of strain-dependent energy barriers. As suggested by this model for soft glassy gels, the Laponite sample seems to behave as an elastic medium, which relaxes to equilibrium after the application of a stress through micro-collapse events. The observed relaxation of the dynamics after flow cessation is thus coherent with the presence of an arrested (gel) phase during the flow in the unsheared band.

The investigation of the system dynamics in the sheared band has already been described elsewhere [36]. There we monitored, through the same DLS technique,

the evolution of the intermediate scattering functions after a shear flow is applied to a dynamically arrested Laponite sample. The same qualitative behavior is observed in the form of the correlation functions and in their evolution with t_w . This result seems to be in contrast with the models describing shear localization in soft-glassy materials [22, 23], where a dynamical transition is expected: in such models, the unsheared band is characterized by an arrested dynamics, while the sheared band exhibits a liquid-like behavior. In the Laponite sample instead, the dynamics relaxation observed in the sheared band after flow cessation suggests the presence of a gel phase, as observed in the unsheared band. The problem may be solved by supposing that, though the sample is sheared, aggregates of gel phase, larger than the scattering volume ($\sim 100 \mu\text{m}$), exist and slip one over the other during the flow. After shear, the dynamics in the scattering volume would thus be characterized by a gel behavior also in the sheared band. Further experiments should be made to clear up if such nonhomogeneous flow is effectively present in the sheared band.

Results II. Oscillations in the flow behavior

Here we report about the observation of periodic oscillations of the shear banding velocity profile, exhibited by very old samples. By monitoring the evolution of the particle velocity through heterodyne DLS, at different positions along the gap, we are able to rebuild the two extreme profiles among which the system oscillates. An example is represented in Fig. 3, where is evident that the velocity profile oscillates among a configuration where the shear is localized next to the rotating plate and a configuration with a linear profile. Most of the time, the system lies in an intermediate profile between the two. The oscillation period is larger than the disk rotation period and remains constant on the timescale of the hours.

Periodic oscillations of the flow behavior when shear localization occurs have been predicted by the phenomenological model presented in Ref. [23] and are here observed for the first time by directly accessing the velocity profile with a high enough time resolution. In the theoretical model, such behavior is interpreted as a stick-slip phenomenon: when shear localization occurs, a diverging viscosity characterizes the unsheared band, which thus slips on the wall; while in the linear profile configuration, the system has a liquid-like behavior and sticks on the wall.

Conclusions

Summarizing, the investigation of the shear localization phenomenon on a Laponite sample have provided

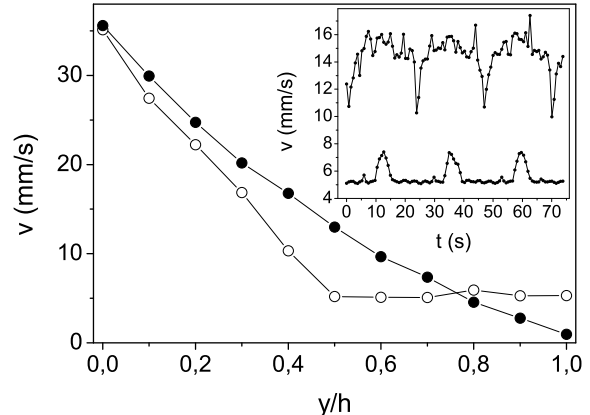


FIG. 3: A global shear rate $\dot{\Gamma} = 4.5 \text{ s}^{-1}$ is applied to a very old Laponite sample and the velocity profile is observed to oscillate between the two extreme profiles plotted. The time period is $T \simeq 23 \text{ s}$. In the *inset*, the oscillations of the particle velocity when the scattering volume is at $y/h = 0.4$ (top) and $y/h = 0.7$ (bottom) are plotted. The small and fast oscillations visible in the bottom curve of the inset have the same period of the disk rotation $T_{rot} \simeq 4 \text{ s}$. They are due to a slight misalignment of the rotational axis (with respect to the orthogonal to the window plate), which induces a small oscillation of the gap width ($\sim 8\%$).

two main results: *i)* through homodyne DLS, the relaxation of the structural dynamics has been followed in the unsheared band soon after flow stop and a stress relaxation behavior, typical of a gel phase, has been evidenced; *ii)* through heterodyne DLS, periodic oscillations of the shear banding profile, reminiscent of a stick-slip phenomenon, have been observed. Taking into account both the oscillating flow behavior and the stress relaxation mechanism, our experimental results strongly support the elastoplastic model proposed in Ref. [25] to describe the flow behavior of a yield stress fluid. Two generic ingredients build up the model, leading to a complex spatiotemporal behavior of the system: local plastic events occur above a microscopic yield stress and nonlocal elastic release of the stress follows [27]. At low shear rates, an intermittent flow localization emerges, with spatially correlated structures forming parallel to the walls; while at high shear rates the flow is homogeneous. The stress relaxation behavior and the oscillating flow localization that characterize this model have both been observed in our experiments on a Laponite sample. This suggests that such elastoplastic mechanism takes place in the sample, and our two main results may be interpreted as two different aspects emerging from this mechanism.

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